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Investigation of sol-gel derived Indium tin oxide thin films with poly(ethylene glycol) as an additive

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Indium tin oxide (ITO) thin films, with/without poly(ethylene glycol) (PEG) additive, were deposited on either glass or oxidized silicon substrates by a sol-gel process. How the morphological, structural, optical, and electrical properties of the resulting ITO films changed with different processing parameters (heat treatment temperature and processing time), were investigated. X-ray diffraction (XRD) results showed that the introduction of PEG lowered the intensity peaks as compared to those from the undoped ones. SEM and AFM investigations indicated that the PEG-doped thin films also result in a flatter surface compared to the undoped. Electrical and optical testing revealed that the doping of PEG could lead to an increased optical transmittance rate (~3-5%) for wavelengths 350-700 nm and a decreased sheet resistance. The ITO thin films prepared at low temperature has been employed as a gas-sensitive material for poisonous gas detection.

Key words: sol-gel, PEG doping, optical properties, electrical properties, indium tin oxide.

Introduction

Indium tin oxide, commonly referred to as ITO, is a useful semiconducting oxide for electronic applications. For example, ITO can be employed as an n-type semiconductor with a band gap between 3.5 and 4.3 eV and a maximum charge carrier concentration in the order of 10^{21} cm^{-3} [1, 2]. Recently, indium tin oxide has also become important as an absorbent for gas sensors [3-5]. Overall, the material properties of ITO are decided by the application requirements.

Since the optical, electrical and other properties of ITO films are highly dependent on the preparation conditions, many methods of preparation including reactive electron beam evaporation, DC magnetron sputtering, thermal evaporation, reactive thermal deposition, spray pyrolysis, laser ablation and more recently sol-gel method have been developed. Among them, the sol-gel process is a promising solution-based process for preparing almost all materials, especially for ceramics and oxides [1, 4-9]. The exploration of sol-gel ITO techniques in the present research is due to its advantages with respect to other routes, such as arbitrary coating on different shapes or areas, high purity, homogeneity without using expensive and complicated equipment, easy control of doping species/dopding level and a relatively low temperature. Moreover, ITO sol-gel technique is compatible with integrated circuits/ microfabrication processes, enabling us to integrate it with other materials/processes. In terms of incorporating with other materials/processes, the processing conditions should be chosen carefully. For example, when an ITO thin films is used for gas sensing, the gas sensor is featured with an ITO thin film of ~100 nm as the receptor to sense the toxic gas and a quartz crystal with a frequency of 10 MHz as a transducer to transfer the surface reactions (mass loading, etc) into a frequency shift [3]. In this application, the processing temperature is a key factor and should be controlled below (<500°C).

Investigations have shown that some polymer additives, like poly(ethylene glycol)($(CH_2\text{-}CH_2\text{-}O)_n$-H), PEG), effectively improve the materials properties at relatively low temperatures [9-14]. Unfortunately, to our knowledge, such an approach had seldom been employed in ITO preparation.

The purpose of the research described here was to prepare ITO thin film for a gas sensing application by means of a sol-gel technique and to investigate the behavior of the resultant ITO thin films under different conditions. First, 10% Sn-doped sol-gel ITO solutions with a variation n the amount of polymer poly(ethylene glycol) (PEG) as additive were prepared and the thin films were deposited by a spin coating technique. Next the optical, electrical, structural and morphological properties were characterized with various techniques. Eventually the results could be used to study the ITO-coated quartz crystal microbalance (QCM) as a gas sensor and provide knowledge of the gas sensing mechanism [3].

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Experimental

Raw Materials

A Sol-gel indium tin oxide solution was prepared from inorganic metal salts of anhydrous indium trichloride powder ($InCl_3$, purity, 99.999%) and tin (IV) chloride ($SnCl_4$, purity, 99.999%). Absolute ethanol and acetylacetone were employed as solvents. All of these chemicals were purchased from Sigma-Aldrich (USA) and used in the as-received state.

Oxidized (100)-oriented silicon wafers and microscopic glass slides were used as the substrates.

Sol-gel & Thin Film Preparation

In general, the starting materials for sol-gels are the class of materials known as metal alkoxides. However, metal organic compounds such as indium and tin alkoxides are very difficult to obtain due to preparation problems, unavailability or high cost. Therefore, inorganic metal salts namely indium trichloride and tin (IV) chloride with appropriate organic solvents provide a viable alternative as the starting materials in the preparation of the "sol" for the ITO thin films.

Figure 1 shows the overall flow-chart for ITO thin film preparation. 3 g anhydrous indium trichloride powder ($InCl_3$) and 22.61 ml acetylacetone were mixed at room temperature and then refluxed at 60°C until the indium trichloride was completely dissolved. The details of the preparation can be found elsewhere [1, 4, 14]. Once the sol is ready, the additive, polymer poly(ethylene glycol) (PEG) with a molecular weight of 400, was added to one part of this solution and othe PEG doped sol-gel solution obtained. Both kinds of sol-gel solutions were further agitated for 60 minutes and finally held at under room temperature for at least one day for stabilization and aging.

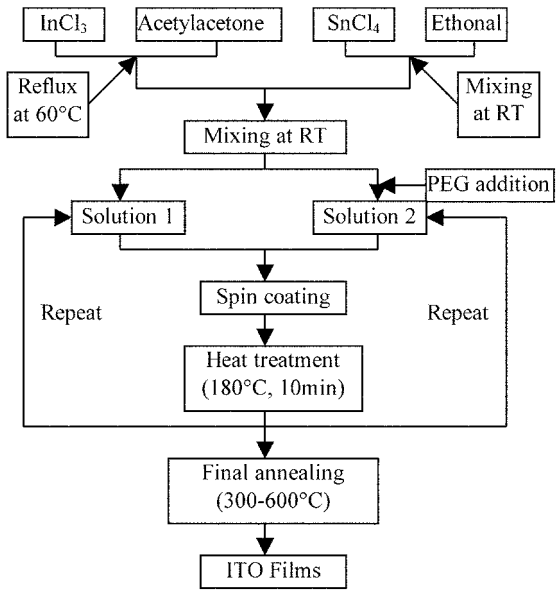


Fig. 1. A flow-chart for ITO thin films preparation.

Spin coating was performed in a cleanroom (Class 100). Before coating, the glass or silicon substrates were cleaned carefully with acetone, isopropanol and subsequently with deionised water, and dried with nitrogen [3]. Before coating, the ITO sol solution was filtered through a syringe equipped with a 0.2 μm filter.

The coated substrates were then prebaked at 150°C for five to ten minutes after each coating. By repeating the above procedure three times, four layers of indium tin oxide film were obtained. A final annealing was performed in air with different times from 30 to 70 minutes and with different temperatures, including 250°C, 300°C, 350°C, 400°C, 425°C, 450°C, 475°C and 500°C.

ITO Thin Films Characterization

– Thickness Determination

The thickness of ITO thin films was measured using a surface profiler. Etching (with photoresist as a mask and 1.5 wt% HBr as etchant) was first performed to create a step (the difference in thickness between the ITO coating and the substrate) for the surface profiler. The thickness of the ITO thin film coating was then determined by measuring the step height.

– X-ray Diffraction (XRD)

The structures of ITO thin films were determined by X-ray diffraction (XRD) with a Bruker X-ray Diffractometer (equipped with a 2D detector) in the reflection mode. The scan parameters were a grazing incidence angle of 1°, and a step size of 0.02°. Testing was carried out with 2θ scanned between 20° to 60° (where most of the diffraction peaks in the indium tin oxide occurred) [2] at a scanning rate of 1°/minute using nickel filtered $CuK_{\alpha 1}$ radiation (λ = 0.15418 nm) at a voltage of 40 kV and a current of 40 mA.

– Scanning Electron Microscopy (SEM)

The surface morphologies of sol-gel ITO thin films were studied using a JEOL JSM 6700F SEM. The ITO thin films were mounted on sample holders with double-sided carbon tape and secured with another layer on top of the thin films to conduct away any charge generated [2]. The films were made more conductive by sputtering a thin layer of conductive material (gold) in argon gas.

– Atomic Force Spectrometry (AFM)

Atomic Force Spectrometry (AFM) measurements were made in multimode with a Nanoscope III controller from Digital Instruments. The images were created in tapping mode using commercial Tapping Mode Etched Silicon Probes and a 10×10 μm^2 scanner. All measurements were performed on areas up to 2×2 μm^2 under ambient conditions [4].

– UV-Visible Spectrophotometry

The optical characteristics of ITO thin films on glass substrates were measured by a Shimadzu UV-2450 UV-visible spectrophotmeter. Single beam scanning was used for the measurement of wavelength ranging from

200 to 700 nm. During measurement, the spectrum was adjusted using a bare glass substrate as an optical reference. The uncoated glass substrate was then placed in the path of the measuring beam for calibration followed by a glass substrate coated with ITO thin film. The resulting signal recorded represents both the ITO thin film and the baseline.

– Electrical/Hall Effect Measurement

The sheet resistance values of ITO thin films were measured using a four-point probe method and the charge carrier concentration was determined by the Van der Pauw method. The sheet resistance and charge carrier concentration were calculated from the average of four measurements for each film. In this work, the electrical properties (sheet resistance and carrier concentration) of ITO thin films were determined using the Van der Pauw method on a HL55WIN Hall System. Square-coated ITO thin film samples were used without additional sample preparation.

Results and Discussion

Preparation Conditions of sol-gel ITO

The preparation conditions for the PEG-doped and undoped ITO thin films are summarized in Table 1. The preparation flow chart is shown in Figure 1.

ITO Thin film characterization

– Thickness Determination

The thickness of 30 wt.% PEG doped ITO thin films, annealed under different conditions, was found to range from 120-140 nm, which is slightly larger than the undoped ones under the same preparation condition, 100-120 nm. The addition of PEG did not increase the thickness of ITO thin films markably although this addition will increase the viscosity of the ITO sol.

– XRD Analysis

• Addition of polymer PEG

Figure 2 shows the XRD spectra of ITO films with 30% PEG annealed at 400°C for 40 minhutes annealing duration as compared to an ITO film without doping (annealed at 400°C for 40 minutes). All spectra showed that ITO thin films (undoped and PEG doped) had only one phase with a rhombohedral structure. The PEG doping did not change the locations of the diffraction peaks. From the XRD spectra, relatively higher and sharper peaks (2θ=30.672°, 35.577°, 51.152° and 60.843° respectively) were observed for the undoped ITO thin film. The addition of PEG resulted in relatively lower peaks from the thin films, indicating that the PEG doping, more or less, can affect the ITO structural properties. However, it seems that the longer annealing time can compensate or enhance the structural properties. This was identified by the appearance of sharper peaks for a sample after 70 minute annealing.

Table 1. Preparation conditions of sol-gel ITO doped with 30 wt.% PEG

Atomic Ratio of In: Sn	10:1
Substrate Temperature	Room Temperature
Mass of indium trichloride ($InCl_3$) used	3.05 g
Volume of tin chloride ($SnCl_4$) used	0.16 ml
Volume of acetylacetone used	22.6 ml
Volume of ethanol used	2.3 ml
Mass of polymer PEG as additives	1.04 g (30 wt.%) (optional)
Annealing Temperature	400°C-600°C
Annealing Time Intervals	30-70 minutes
Layers of coated ITO Thin Film	4

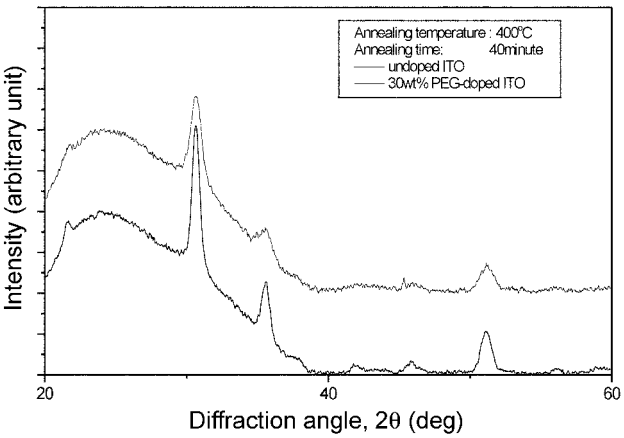


Fig. 2. A X-ray diffraction (XRD) spectra of indium tin oxide doped with 30 wt% PEG deposited on glass for different annealing time intervals annealed at 400°C as compared to that of the undoped ITO thin film.

The influences of annealing temperature on the structural properties were also investigated by checking the XRD spectra of samples annealed at 500°C and 600°C. It was found that the higher annealing temperature can effectively increase the structural properties.

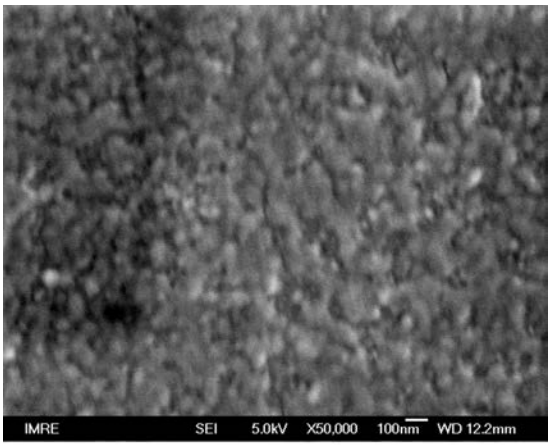
– Scanning Electron Microscopy (SEM)

The surface morphologies of PEG doped ITO films were observed by SEM. Figure 3(a) and (b) show the SEM micrographs of ITO thin films annealed at 450°C for 50 and 70 minutes, respectively. From the SEM figures, cracking-free, uniform and compact ITO thin films under different magnifications were observed although it was possible that some microscale porosity was present in the films [6]. In addition, it was noted that the longer annealing duration lead to a finer particle size and lower porosity. The doped samples had finer crystalline particles compared with the undoped ones(these pictures are not shown here).

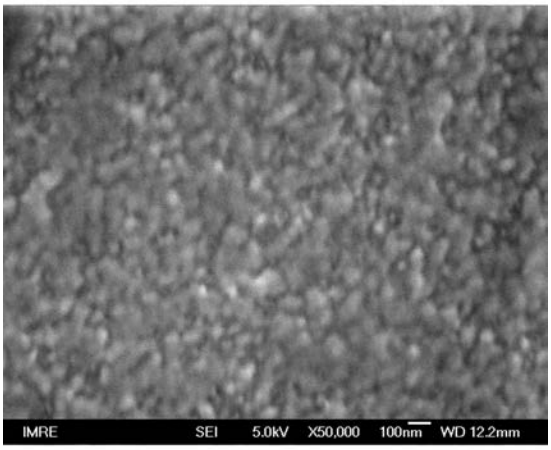
– Surface Morphology

• Addition of polymer PEG

Figures 4 and Figure 5(a-d) showed the evolution of surface roughness of ITO thin films without (in Figure 4) and with 30 wt% PEG (in Figure 5(a-d)) deposited on glass substrates and annealed under different temperature and time by atomic force microscopy (AFM) (with a scanning area of 2 μm × 2 μm). The ITO film



(a)



(b)

Fig. 3. SEM pictures for the undoped (a); and PEG-doped samples (b) undergoing the annaling at 400ºC for 1 hour.

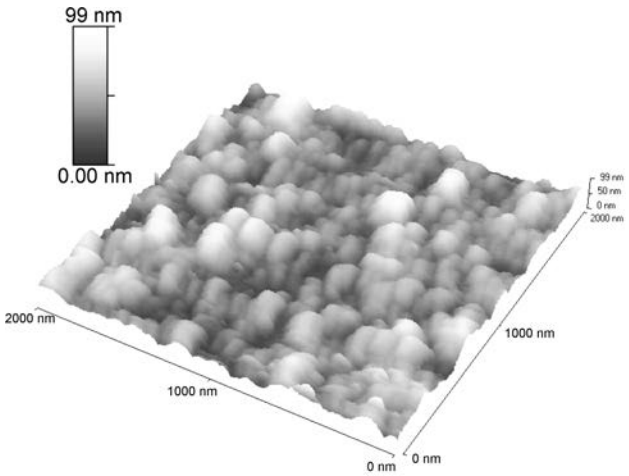


Fig. 4. AFM image (2 μm × 2 μm) of the ITO thin film deposited on glass substrate annealed at 600ºC for 50 min.

without PEG doping had a surface roughness ~15 nm. The root-mean-square (RMS) surface roughness values of ITO films with PEG doping were approximately 10, 8, 9 and 5 nm under the different conditions given in Fig. 5(a-d) respectively. From these images, it was noted that finer-grained surface features of ITO thin films were observed with an increase in either annealing temperature or time. Thus, the results showed that higher annealing temperatures and longer annealing time improved the surface roughness of ITO thin films.

In addition, in comparison with Fig. 4, it was noted that the PEG-doped ITO films provided a relatively lower RMS value than that of the undoped ones (~15 nm) even though the films were prepared at a relatively high temperature (~600ºC). This observation showed that the addition of PEG to ITO thin films had further improved the surface roughness in addition to the effect of the annealing conditions mentioned above.

– Electrical Properties-Sheet Resistance

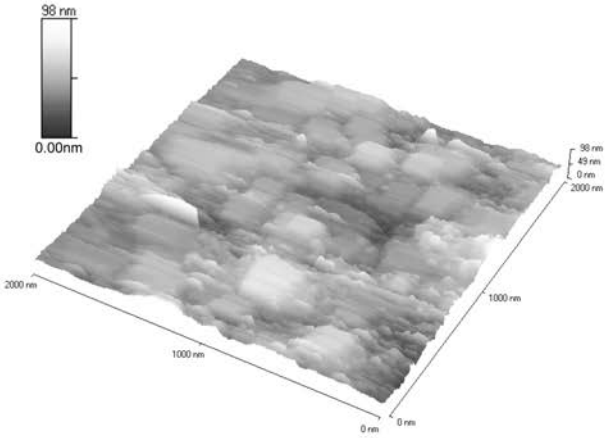
The annealing temperature was found to affect the electrical properties of ITO thin films greatly. Figure 6 shows the sheet resistance of 30 wt.% PEG doped ITO films as a function of annealing temperature. It was observed that the sheet resistance of ITO thin films decreased from 6.23±0.1 to 4.28±0.01 as the annealing temperature increased from 400ºC to 600ºC. The resistance decreased significantly from 6.23±0.1 to 4.55± 0.75 as the annealing temperature was increased from 400ºC to 450ºC. A similar trend was observed for different annealing times. The minimum sheet resistance of ITO films was found to be 6203 Ω/sq units for a sample annealed at 600ºC for 70 minute. The decrease in sheet resistance with increased annealing temperature may be explained by the fact that the crystallite size of the ITO thin films increased with increasing annealing temperature, thus reducing the grain boundary scattering and enhancing conductivity [5, 6].

– Optical properties -Transmittance rate

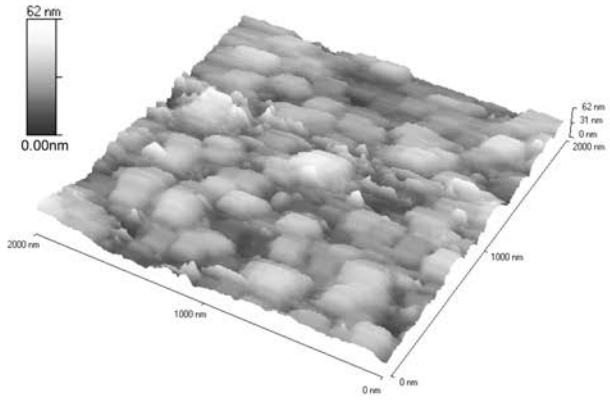
Figure 7 shows the results of undoped PEG samples annealed at 400ºC for different times. It can be seen that the annealing time does not affect the optical transmittance rate. In all cases, the transmittance rate is ~80% in the visible wavelength (400-700 nm). Figure 8 shows the transmittance rate results of PEG doped and undoped samples. It can be seen that after the PEG doping, the optical transmittance rate in the visible range can be enhanced by ~3-5% in the wavelength range of 350-550 nm. In addition, it is evident that there is a blue shift at the ultraviolet adsorption edge. This change can be explained by the intensity enhancement of the Burnstein-Moss shift, which are caused by the increase of the carrier concentration upon crystallization [15].

Discussion

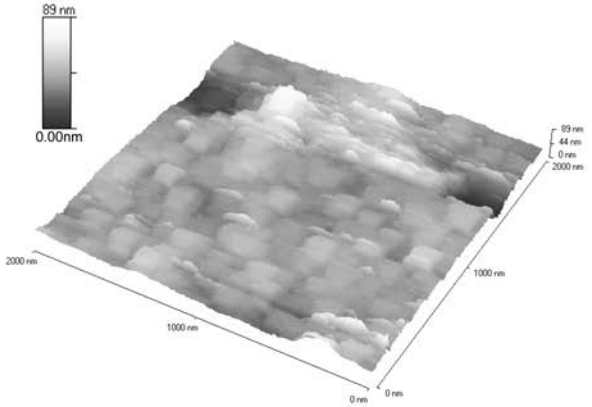
XRD results showed that sharper peaks were obtained at higher annealing temperatures and longer annealing times. The doping by PEG in ITO thin films resulted in relatively lower diffraction peaks and degraded structural properties. The SEM results showed uniform and compact doped ITO thin films devoid of



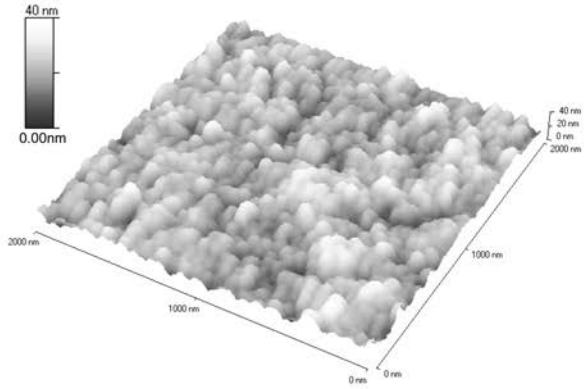
(a) AFM image (2 μm x 2 μm) of an ITO thin film doped with 30 wt. % PEG deposited on a glass substrates annealed at 400°C for 50 minutes.



(b) AFM image (2 μm x 2 μm) of an ITO thin film doped with 30 wt. % PEG deposited on a glass s ubstrate annealed at 400°C for 70 minutes.



(c) AFM images (2 μm x 2 μm) of an ITO thin film doped with 30 wt. % PEG deposited on a glass substrate annealed at 500°C for 70 minutes.



(d) AFM image (2 μm x 2 μm) of an ITO thin film doped with 30 wt. % PEG deposited on a glass substrate annealed at 600°C for 50 minutes.

Fig. 5. (a), (b), (c), (d) AFM images (2 μm × 2 μm) of ITO thin films doped with 30 wt% PEG deposited on glass substrates annealed under different conditions (600°C for 50 min).

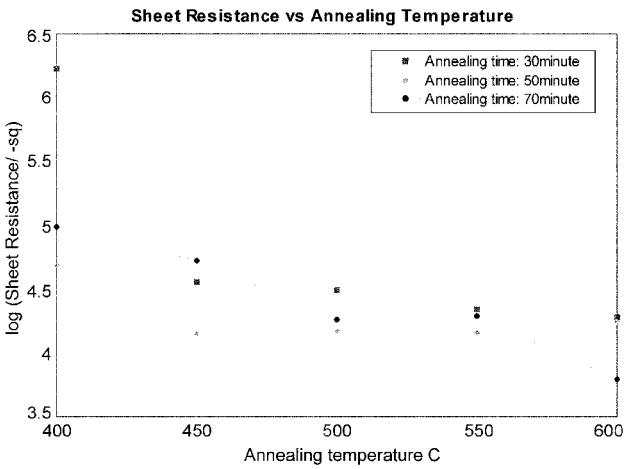


Fig. 6. Sheet resistance of ITO thin films doped with 30 wt.% PEG as a Function of annealing temperature annealed in air for 30 minutes.

any cracks. AFM measurements showed that the surface of the undoped ITO thin film was rather rough (RMS ~15 nm). The addition of PEG to ITO thin films enhanced the surface roughness and a RMS value of as low as approximately 5 nm was obtained under the same preparation conditions. Thus, increasing the temperature and time enhanced the surface morphology, leading to a finer particle size and lower porosity of doped ITO thin films.

The optical transmission of the undoped ITO thin films annealed between 400°C and 500°C in air was approximately 80% (wavelength of 450 nm-700 nm) as compared to the uncoated glass. The optical properties of ITO thin films became less dependent on the annealing temperature and time when the heat treatments were performed above 400°C. The decrease in annealing temperature reduced the total transmission of the ITO thin films. The increase in optical transmission

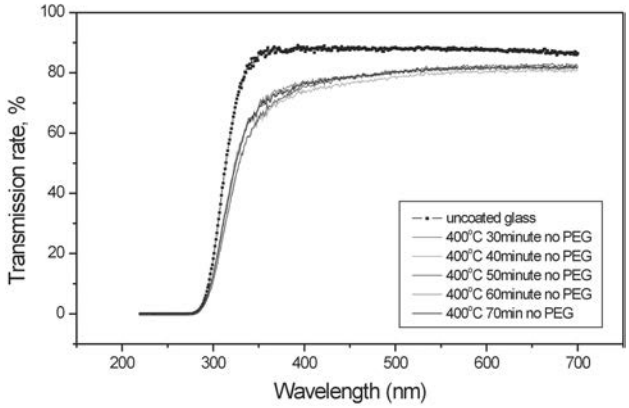


Fig. 7. Optical transmission spectra of undoped ITO films (100 nm) with different annealing temperature ranging from 250°C to 500°C annealed for 30 minutes.

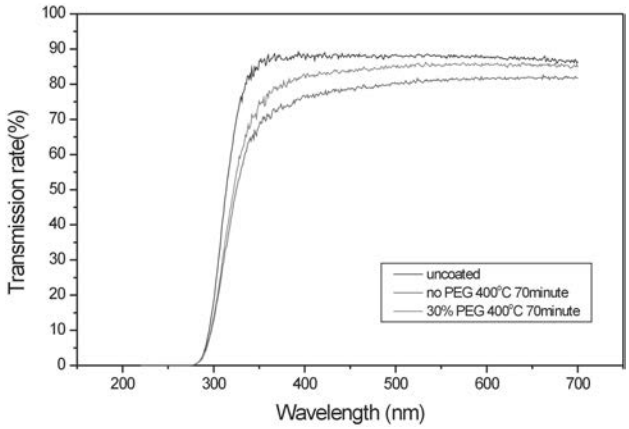


Fig. 8. Comparison of transmittance rate for the samples with/ without the PEG doping.

with annealing temperature can be attributed to an increase of structural homogeneity and crystallinity. The addition of PEG to ITO thin films was found to improve the optical transmission of ITO thin films and a relatively higher transparency of 90%, as compared to that of the uncoated glass, was obtained.

The PEG doping will result in the cracking-free films with improved surface roughness, optical transmittance rate and a decreased electrical resistance. However, the thickness of the films was hardly influenced by the addition of PEG if the molecular weight was not too high.

In principle, the optical property enhancement of PEG-doped thin films can be attributed to two aspects: fine crystallinity or less scattering. From the XRD results, we note that the crystallinity of PEG-doped samples is not be improved greatly. By contrast, the orientation of the films is degraded a little. So the improved optical properties is mainly attributed to the decreased scattering due to the improved surface roughness. Since the PEG additive can avoid particle aggregation occurring in the sol-gel solution, the PEG-doped thin films have fine crystalline particles and thus decrease the scattering existing in the crystallite boundaries.

Conclusion

Indium tin oxide (ITO) thin films with polymer poly (ethylene glycol) (PEG) as additives have been deposited on glass substrates by a sol-gel process using low cost, inorganic metal salts (anhydrous indium trichloride and tin (IV) chloride). Various properties of ITO thin films have been prepared and characterized. The doping of PEG in ITO thin films can enhance various properties of the films, such as decreasing surface roughness, lowering the sheet resistance, increasing the optical transmittance rate, etc, although the doping can slightly degrade the structural properties. These results obtained can be used to prepare a functional material for a gas sensor.

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